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Title: STUDIES OF HYDROGEN PRODUCTION BY THE WATER GAS SHIFT REACTION AND RELATED CHEMISTRY

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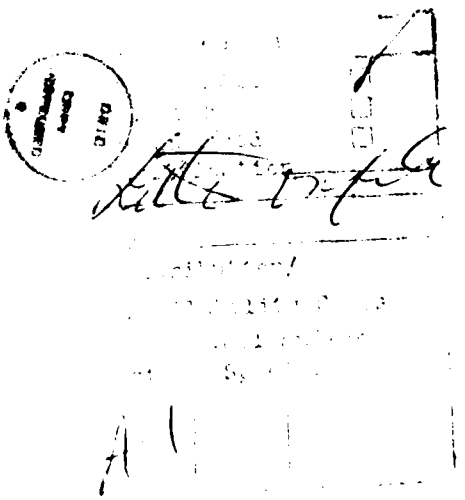
Abstract

Many systems have been investigated for the catalysis of the water gas shift reaction, $H_2O + CO \rightleftharpoons H_2 + CO_2$, and for electrocatalytic oxidation of CO, $CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^-$. These systems have involved precious metal complexes composed of Pt, Rh, and Ir, and reaction conditions for these systems have been especially mild: atmospheric pressures and low temperatures (80 - 100°C). In addition aqueous acidic conditions for these systems have been pursued with particular interest in adopting water gas shift catalysts to act as electrocatalysts for the anode reaction of CO fuel cells. Under these conditions the best water gas shift catalysts observed have been $PtCl_4^{2-}$-$SnCl_4$-$SnCl_2$, trans - $PtCl_2(SnCl_3)_2^{2-}$, $[Rh(CO)_2Cl]_2$, $Rh(CO)_2Cl_2^{2-}$, $PtCl_4^{2-}$-$PbCl_2$, and $PtCl_3(C_2H_4)^-$. None of these electrocatalytically oxidized CO; however, $RhCl(PPh_3)_3$, $Rh(dppe)(mnt)^-$, and $Rh(dppe)_2^+$, complexes known to bind CO, did exhibit some limited electrocatalytic CO oxidation behavior.



Objectives of the Study

The present study was undertaken in order 1) to gain a better understanding of homogeneous water gas shift (WGS) catalysis and of homogeneous CO oxidative electrocatalysis in aqueous acidic media under mild conditions, and 2) to develop and design homogeneous catalytic systems which might lead to greater catalytic efficiency and which would delineate factors leading to further understanding of WGS catalysis and CO electrocatalysis.

The primary focus was on the use of homogeneous catalytic systems because homogeneous catalysts have a number of advantages over heterogeneous catalysts when fundamental chemical information is sought. These advantages are: 1) homogeneous catalysts exhibit greater efficiency and selectivity of reaction than do heterogeneous catalysts, and usually operate under milder conditions, 2) through systematic variation of complexed metal ion(s), coordinating ligands, and solvent systems, great flexibility exists in design of homogeneous catalysts, and 3) the study of homogeneously catalyzed reactions can be performed using established physical and spectroscopic methods.

The objective of employing aqueous acidic media to study WGS catalysis was prompted by a number of factors. First, the primary investigator has shown that WGS catalysis can occur under these conditions. Second, the media are simple, allowing CO_2 production to be followed readily while avoiding the stoichiometric consumption of base. Third, acidic electrolytes are most commonly used in hydrocarbon-air fuel cells and are well suited to oxidative electrocatalysis.

Introduction

The WGS reaction, eqn. (1), has been known and studied for over 75 years. Its significance derives from its role in the preparation of ammonia synthesis gas

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \quad (1)$$

and from its ability to increase the H_2:CO ratio in gaseous feedstock for methanation and Fischer Tropsch synthesis.[2] Its importance for the reduction of nitrogen and sulfur oxides in the treatment of combustion exhausts has also been recognized.[3]

Closely related to the WGS reaction is the CO oxidation half-reaction, eqn. (2). The importance of this reaction stems from the development of portable

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^- \quad (2)$$

fuel cells which use readily available fuels such as gasoline and related hydrocarbons and which generate CO and CO_2 as oxidation end products of anode reactions. Unfortunately, CO poisons these systems and reduces the efficiency of the hydrocarbon-to-electricity conversion.

Thermodynamically, reaction (1) is favored under ambient conditions (ΔH^o_{298} = +0.68 kcal/mole; ΔG^o_{298} = -4.76 kcal/mole; E^o = +0.10V). But like most reactions, kinetic barriers are large and the reaction only proceeds either at elevated temperatures and/or in the presence of suitable catalysts. Commerical catalysts for (1) are heterogeneous, based mainly on $Fe3O_4$ and related oxides, or on Cu and Cu-Zn mixtures.[1] These systems operate at temperatures of 300-350°C and 200-250°C, respectively. There are no known commerical electrocatalysts for (2).

Attempts to catalyze the WGS reaction homogeneously can be traced back to studies by Hieber[(4)] in 1932 on iron carbonyl, carbonyl hydrides, and carbonyl hydride anions. The reaction of $Fe(CO)_5$ with aqueous base, eqn. (3), was observed to result in the oxidation of CO to CO_2 and the reduction of H^+ to coordinated

hydride. Further reaction of the product CO_2 with base produced carbonate. Acidification of the $HFe(CO)_4^-$ produced resulted in the formation of an

$$Fe(CO)_5 + 2OH^- \longrightarrow HFe(CO)_4^- + HCO_3^- \quad (3)$$

unstable dihydride which liberated hydrogen. Regeneration of the starting complex by CO addition completed the cycle, and the WGS reaction was achieved in principle. The problem, however, was that (3) required strong base which was consumed stoichiometrically in the catalytical cycle. Further studies[5] produced no solution to this problem until 1977, when Ford and coworkers[6] were able to catalyze (1) homogeneously using $Ru_3(CO)_{12}$ in alkaline ethoxyethanol. Although the rates of reaction were slow, stoichiometric base consumption was avoided because the $KHCO_3$ produced was unstable in ethoxyethanol under the reaction conditions, and decomposed to give CO_2 and the starting base, KOH. Subsequent to Ford's initial report, he and others[7-9] have described successful catalysis of (1) using a variety of metal carbonyls and carbonyl cluster compounds in basic media. Ford et al.[7] have also reported that mixed metal systems, based e.g., on $Ru_3(CO)_{12}/Fe(CO)_5$ and a change to acidic media increase the rates of catalysis significantly. Fenton described WGS catalysis under more forcing conditions (56atm CO and 200°C), and a recent report demonstrated WGS catalysis by a Ru complex immobilized in a zeolite matrix.[11] Other studies have also described the use of the WGS reaction in situ to promote the transformation of organic substrates.[8,12-15]

The electrocatalytic oxidation of CO in aqueous media is less well established. Pletcher[16] and Breiter[17] have described Pt catalysts which electrocatalytically oxidize CO, and alloys of Pt[18] and Pd[19] have been shown to catalyze CO electro-oxidation. In these cases the reaction is thought to occur via a reactant pair mechanism.[20] Gilman[20] describes this mechanism as a reaction between adsorbed CO and an oxidized Pt species or, in the case of alloys, an oxidized second metal

species. van Baar, van Veer, and deWit[21] have found that CO is electrochemically oxidized by untreated and heat treated carbon-supported Rh and Ir porphyrins at room temperatrue in acidic electrolyte. These investigators envision that the CO oxidation occurs at a single metal ion with the activation of the CO ligand toward nucleophilic attack being achieved through coordination to a metal ion in a higher oxidation state. As one might suspect, this mechanism has been proposed previously with respect to the WGS reaction.[22] Recently, Hollenberg, Cole, and Kubiak[23] have discovered that using a $HFe(CO)_4^-$ based system electrocatalytic CO oxidation results with an efficiency for the conversion of chemical energy into electrical energy of 67-80%.

Interest in homogeneously catalyzing the WGS reaction and the electrooxidation of CO derived from several notions. First, the WGS reaction is relatively simple, and precedents for component parts of the reaction using metal complexes are abundant in the literature. Equation (4) represents the well known reduction of

$$M^{n+} + CO + H_2O \longrightarrow M^{(n-2)+} + CO_2 + 2H+ \qquad (4)$$

metal ions by CO. The similarity between eqns.(2) and (4) is apparent. Thus, WGS catalysts could serve as electrocatalysts for CO oxidation. Second, because of the simplicity of the WGS reaction, its catalysis can serve as a model for activating CO toward reduction, which is more difficult to catalyze homogeneously.[25] This is true despite the fact that (1) involves CO oxidation and not reduction, because in either case the oxidation state change occurs at carbon, necessitating attack at that position. Third, homogenous catalysis is usually carried out at relatively low temperatures which favors product formation in the WGS reaction and CO oxidation half-reaction.

The Plan

General Methods for WGS Studies. The catalyst system under investigation was prepared by dissolving the catalyst in a desired acid (~25ml) and adding a concentrated mineral acid (~5ml) and H_2O (5ml). This solution was then placed in a 1ℓ single-neck round bottom flask (reaction vessel) which had a three-way stopcock connected to it via a side-arm. One stopcock lead was connected to either a vacuum or gas source, and the second lead was cut short, stoppered with a serum cap, and used for gas sampling. A ground glass adaptor connected the vessel to a Hg manometer. After preparation the systems were degassed by three flush-pump cycles with CO, filled with the desired amount of CO (usu. 200-600 torr) and CH_4(~100-200 torr, used as an internal standard), and heated to the desired temperature (usu. 80-100°C) in an oil both such that the solutions were immersed to the level of the side-arm.

Separation of gases (H_2, CO, CH_4, and CO_2) was achieved by gas chromatography (GC) on a Porapak Q column. The column was calibrated by connecting an empty reaction vessel to a Hg manometer and purging with the desired gas several times. The vessel was then filled with the gas, the system pressure recorded, and a 0.5ml gas sample analyzed by GC. The system pressure was reduced by momentary application of vacuum, another sample taken, and the process repeated. Linear plots of peak area vs. partial pressure were obtained. For the catalyst systems 0.5ml gas samples were analyzed periodically and from the calibration curve and the CH_4 internal standard the amounts of reactant and product gases were determined.

General Methods for Electrocatalytic Studies. The catalyst under investigation was dissolved in a suitable solvent with excess supporting electrolyte present in a 100 or 250ml three-neck round bottom flask which had two 1-way stopcocks connected to it via sidearms. From the necks of the flask were supported

the reference electrode, working electrode, and auxiliary compartment and electrode via ground glass adaptors or tightly fitting rubber stoppers. Gases (Ar,CO) were purged into the vessesl through the 1-way stopcocks and the lead from one of the stopcocks was stoppered with a serum cap and used for gas sampling. The reference electrode was a saturated calomel electrode (SCE) and the working electrodes were either platinum or glassy carbon. Because the Pt electrodes were poisoned by CO, in many studies glassy carbon electrodes were used for both voltammetry and electrolyses. The auxiliary electrode was Pt and was placed in an auxiliary compartment which contained the same solvent and supporting electrolyte as the material under investigation and which made contact to the main compartment and solution through a disc of vycor glass.

Cyclic voltammograms of the catalyst systems were recorded under Ar initially. Then the systems were purged with CO and cyclic voltammograms were again recorded. For those systems which, after CO purging, exhibited either more intense anodic waves or new anodic waves at lower potentials, controlled potential oxidations at the peak of the waves under 1 atm CO were carried out. The amount of charge passed during an oxidation was monitored with a digital coulometer and the reactant and product gases were analyzed by GC by removing a 0.5ml gas sample and injecting it into a Porapak Q column. The calibration curves from the WGS studies were used to determine the amounts of gases.

Results and Discussion

Water Gas Shift Catalysis. Catalysis of the WGS reaction in aqueous acidic conditions has been observed only with the following catalyst precursors and conditions: 1) $PtCl_4^{2-}$-$SnCl_4$ in HOAc/HCl/H_2O; 2) $[PPh_4][Rh(CO)_2Cl_2]$ or $[Rh(CO)_2Cl]_2$ in HOAc/HI/H_2O; 3) $PtCl_4^{2-}$-$PbBr_2$ or $PbCl_2$ in HOAc/HCl/H_2O; 4) $Os_3(CO)_{12}$ supported on acidic zeolite in H_2O; and 5) $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, or $Fe(CO)_5/Ru_3(CO)_{12}$ in diglyme/H_2SO_4/H_2O. The first three systems have been observed in this laboratory, the fourth in Granziani's[25] laboratory, and the fifth in Ford's[7] laboratory. Of the systems which we have discovered, the $PtCl_4^{2-}$-$SnCl_4$[26] and $Rh(CO)_2Cl_2^-$ [22,27,28] systems have been reported in the literature. Further studies of the $PtCl_4^{2-}$-$SnCl_4$ system were briefly carried out. The $PtCl_4^{2-}$-Pb systems are new systems which we have recently discovered. Numerous other systems in acidic media were investigated (see Table 1), but most of these systems have very little or no catalytic activity.

WGS catalyses by $PtCl_4^{2-}$-$SnCl_4$ in HOAc/HCl/H_2O is complicated. Only under conditions in which the initial ratio of concentrations of Sn^{IV}:Sn^{II}:Pt^{II} was adjusted to 22-25:2-5:1 did simultaneous and stoichiometric formation of the products CO_2 and H_2 occur; after catalysis ceased, recharging with CO did not always result in 1:1 H_2 to CO_2 formation again. When 1:1 product formation occurred, based on initial rates the formation of both products was roughly first-order with respect to [Pt] and H_2 formation was first-order with respect to p_iCO. In order to gain a better understanding of this system, attempts were made to prepare the proposed catalyst precursors $Pt(SnCl_3)_5^{3-}$, cis-$PtCl_2(SnCl_3)_2^{2-}$, and trans-$PtCl_2(SnCl_3)_2^{2-}$. In no instance was the red $Pt(SnCl_3)_5^{3-}$ obtained by following the literature procedure[29]; after many attempted syntheses only dark orange or orange-yellow materials were isolated by precipitating the anionic species with Bu_4N^+ or Ph_3MeP^+. These materials were believed to be mixtures of

cis- and trans-$PtCl_2(SnCl_3)_2^{2-}$ based on UV-visible spectroscopy and conductivity measurements. The red trans-$PtCl_2(SnCl_3)_2^{2-}$ was prepared by precipitation with Me_4N^+. These materials acted as catalyst precursors for the WGS reaction and nearly identical rates of H_2 and CO_2 formation resulted in their presence with turnover numbers of ∿0.5 and 1.1 mmoles product/mmole complex/h for the cis-trans $PtCl_2(SnCl_3)_2^{2-}$ mixture and the trans-$PtCl_2(SnCl_3)_2^{2-}$, respectively. Unfortunately, these materials did not maintain catalytic activity after being recharged and during the catalytic runs a dark precipitate formed. Because trans-$PtCl_2(SnCl_3)_2^{2-}$ exhibited greater catalytic activity and is the kinetic product during preparation, this complex could be the key catalytic precursor.

When solutions of $PtCl_4^{2-}$ in HOAc/HCl/H_2O in contact with slurries of $PbCl_2$ or $PbBr_2$ were charged with CO, WGS catalysis occurred. The solutions which were initially light red slowly became yellow and after an induction period of 2-3h stoichiometric production of H_2 and CO_2 resulted. After catalysis commenced ($\geq$1h) heterogeneity was observed in the yellow solutions. If the yellow solutions were filtered to remove Pt particles and excess PbX_2, WGS catalysis continued at the same rate with no induction period; but with time heterogeneity was observed. The rate at which these systems catalyzed the WGS reaction depended upon the PbX_2 and p_iCO. With p_iCO = 400 torr, the turnover numbers were ∿1.0 and ∿0.24 mmoles product/mmole Pt/h for the systems in which $PbCl_2$ and $PbBr_2$, respectively, were added as cocatalysts. For the $PtCl_4^{2-}$-$PbCl_2$ system the rate of CO_2 production appeared to be directly related to p_iCO.

From a $PtCl_4^{2-}$-$PbCl_2$ or $PtCl_4^{2-}$-$PbBr_2$ system in which WGS catalysis occurred yellow crystals could be collected by adding excess Bu_4NBr in EtOH to the yellow filtrate and cooling the filtrate to 0°C. The same material was obtained regardless of which cocatalyst was employed because the infrared and ^1H NMR spectra were nearly identical: ν_{CO} 2080cm^{-1};$\delta(CDCl_3)$1.02(t)3H, 1.55(q)2H,1.75(m)2H, 3.25ppm(t)2H.

The ^1H NMR spectrum of this material indicated that only protons due to Bu_4N^+ were present, i.e. no H^- peaks. Presumably this material was $[Bu_4N][Pt(CO)Cl_3]$; it demonstrated no WGS catalysis.

When $PtCl_4^{2-}$ was refluxed in EtOH/HCl over $PbCl_2$ or $PbBr_2$ under N_2, the solution changed from red to yellow. If excess Bu_4NBr was added as in the catalytic filtrates, yellow crystals were obtained. The spectroscopic results for this material were as follows: $\nu_{C=C}$ 1230cm^{-1};$\delta(CDCl_3)$1.02(t)3H, 1.55(q)2H, 1.75(m)2H, 3.25(t)2H, 4.40ppm(m)1H (J_{Pt-H} = 29.5H_2);$\delta((CD_3)_2CO)$ 0.85(t)3H, 1.32(q)2H, 1.70(m)2H, 3.32(m)2H, 4.05ppm(m)1H (J_{Pt-H} = 32Hz). Conductivity measurements indicated that this material was a 1:1 electrolyte, the molecular weight determined by cryoscopy was 615 ± 60g/mole, and the elemental analysis gave an empirical formula of $PtNCl_3C_{18}H_{40}$; thus, the crystals were identified as $[Bu_4N][PtCl_3(C_2H_4)]$ or Ziese's salt. Refluxing $PtCl_4^{2-}$ in EtOH/HCl under N_2 in the absence of PbX_2 did not yield Ziese's salt. Apparently, PbX_2 abstracts Cl^- from $PtCl_4^{2-}$, and in the presence of HCl which dehydrates ETOH, Ziese's salt forms. $PbCl_2$ appeared to abstract Cl^- from $PtCl_4^{2-}$ better than $PbBr_2$:WGS catalysis was more rapid in the presence of $PbCl_2$ than $PbBr_2$ and with $PbCl_2$ the yield of Ziese's salt was greater than with $PbBr_2$, 81% and 60%, respectively, for reactions carried out over the same time period and under identical conditions.

Ziese's salt catalyzed the WGS reaction in HOAc/HCl/H_2O. The yield of CO_2 and H_2 were stoichiometric, no induction period occurred, and the turnover numbers were ∿0.62 mmoles product/mmole Pt/h. With time heterogeneity was observed. When Ziese's salt was placed in HOAc/HCl/H_2O and charged with equal pressures of CO and C_2H_4, olefin hydrogenation resulted as well as WGS catalysis: H_2 and C_2H_6 were reduction products. The yield of reduced products, H_2 and C_2H_6, equaled the yield of oxidized product, CO_2, and the turnover number was ∿0.58 mmoles CO_2/mmole Pt/h.

Electrocatalytic Oxidation of CO. The electrocatalytic oxidation of CO was studied with the WGS catalytic systems, $PtCl_4^{2-}$-Sn and $[Ph_4P][RhCl_2(CO)_2]$, and with precious metal complexes which were reasoned to be possible electrocatalysts. In most cases cyclic voltammetry and electroxidations were accomplished at glassy carbon elecrodes because the Pt electrodes employed in these studies were poisoned by CO. In addition due to the solubility limitations of the possible electrocatalysts many studies were not performed in aqueous acidic media.

Initially the possibility that Pt-Sn systems and complexes could electrocatalytically oxidize CO were investigated. Based on cyclic voltammetry in $HOAc/HClO_4/H_2O$, the addition of $SnCl_3^-$ or $SnCl_4$ and $PtCl_4^{2-}$ to an Ar purged solution resulted only in a weak cathodic wave near the solvent limit for $SnCl_3^-$ at Pt or C electrodes. Moreover, trans-$PtCl_2(SnCl_3)_2^{2-}$ and the cis-trans-$PtCl_2(SnCl_3)_2^{2-}$ mixture were electroinactive at either surface. At a Pt electrode in $HOAc/HClO_4/H_2O$ two irreversible oxidation waves for CO were observed at approximately +1.30 and +1.46V vs. SCE. The Pt-Sn system or cis-and trans-$PtCl_2(SnCl_3)_2^{2-}$ caused no change in the CO oxidation waves which suggested that this system and these complexes are not feasible for electrocatalytic CO oxidation.

The ability of $[Ph_4P][RhCl_2(CO)_2]$ and related complexes to act as possible CO electrooxidation catalysts was studied next. In aqueous acid (HOAc) or nonaqueous (i-PrOH,THF,acetone) solvents, $[Ph_4P][RhCl_2(CO)_2]$ exhibited no oxidation waves at a C electrode under Ar and $[Ph_4P][RhCl_2(CO)_2]$ had no effect on the CO oxidation waves. These observations suggested that $RhCl_2(CO)_2^-$ would not be a feasible CO electrooxidation catalyst; therefore, related Rh complexes which had lower oxidation potentials were investigated for their possible electrocatalytic activity. These complexes were $Rh(CO)_2(mnt)^-$, $Rh(CO)(PPh_3)(mnt)^-$, and $Rh(mnt)(dppe)^-$ and they had oxidation potentials under Ar on a glassy C electrode at +0.75, +0.50, and -0.05V vs SCE, respectively. The ease of oxidation of these materials

($Rh(mnt)(dppe)^-$ > $Rh(PPh_3)(CO(mnt)^-$ > $Rh(CO)_2(mnt)^-$) followed from the σ-donor/ π-acceptor properties of phosphine versus carbonyl ligands. Purging solutions of these complexes with CO resulted in little or no change in the oxidation waves; nonetheless, controlled potential oxidations under CO in i-PrOH or acetone at the peaks of the oxidation waves were performed. No electrocatalytic behavior was demonstrated for $Rh(CO)_2(mnt)^-$ and $Rh(CO)(PPh_3)(mnt)^-$;in the presence of $Rh(dppe)(mnt)^-$ after two days 1.25 torr CO_2 was formed with a current efficiency of ∿73%.

Finally because $RhCl(PPh_3)_3$ and $Rh(dppe)_2^+$ reversibly bind CO, these materials were studied as possible electrocatalysts for CO oxidation. $RhCl(PPh_3)_3$ and $Rh(dppe)_2^+$ had high oxidation potentials under Ar at a C electrode, +1.00 and +0.95V vs SCE, respectively, and the presence of CO had little or no effect on the oxidation waves. Controlled potential oxidations under CO, however, at the peaks of these waves promoted the oxidation of CO to CO_2 at a glassy C electrode, but the processes were slow and required relatively high potentials. For example, with $RhCl(PPh_3)_3$after 60 hours only 0.082 mmoles CO_2 were produced by oxidizing at +1.00V vs SCE from a system which was initially charged with 3.34 mmoles CO; the amount of $RhCl(PPh_3)_3$added to this system was 0.022 mmoles. Due to the high oxidation potentials required and the slow catalytic rates further studies with these complexes were not pursued.

Conclusions and Recommendations

A number of systems in aqueous acidic media have been investigated for WGS catalysis. Of the systems which have been studied only $PtCl_4^{2-}$-$SnCl_4$-$SnCl_2$ (1:22-25:2-5), trans-$PtCl_2(SnCl_3)_2^{2-}$, $PtCl_4^{2-}$-PbX_2,$PtCl_3(C_2H_4)^-$, $[Rh(CO)_2Cl]_2$, and $RhCl_2(CO)_2^-$ acted as genuine catalyst precursors. All of these systems catalyze the WGS at comparable rates (0.5-1.0 mmoles product/mmmole catalyst/h) and the Pt-Sn[30] and $PtCl_3(C_2H_4)^-$ systems have been shown to use the WGS reaction to hydrogenate olefins. For the Pt systems the Pt^{2+}/Pt^0 couple appeared to be important in the catalytic cycle: in many instances heterogeneity or polymer formation (presumably, $[Pt(CO)_x]_y$) was observed after catalysis. Therefore, further studies with these systems should be directed at solubilizing Pt^0 in aqueous acidic media. Strong σ-donor ligands such as phosphines are known to stabilize lower oxidation states and are not acid labile, but complexes such as PtL_4 or PtL_3(L = phosphine) would also be insoluble under the reaction conditions. The study of PtL_3Cl^+ or $PtLCl_3^-$ complexes, however, might be feasible; these complexes might act as entities into the catalytic cycle and maintain solubility at the Pt^0 state.

None of the systems investigated for the electrocatalytic oxidation of CO so far have met with much success. While $Rh(dppe)(mnt)^-$, $RhCl(PPh_3)_3$, and $Rh(dppe)_2^+$ promoted slight CO oxidation, the yields and rates of CO_2 formation were extremely poor. These complexes do bind CO. The systems which demonstrated WGS activity (above) were either electroinactive or inactive as CO oxidation electrocatalysts. None of these systems had redox potentials near the thermodyanamic values for CO oxidation or H^+ reduction; thus, further studies might focus on electrocatalytic precursors which have redox potentials near those for the thermodynamic potentials,and which are known to interact, preferably bind, CO. Moreover,

recent work has demonstrated that WGS catalytic systems can act as CO oxidation electrocatalysts.[23] Though studies in this regard in this laboratory have been unsuccessful, it appears that the approach is viable and should lead to the discovery and development of efficient CO oxidation electrocatalysts.

Table 1

Complex	Conditions	Observations
$Rh(dppe)(mnt)^-$	Triflic Acid/H_2O:4/1 400 torr CO T ∿90°C	Soln. becomes dark upon addition of orange complex; 1.4 torr CO_2 after 2 days, no H_2
$Rh(dppe)(mnt)^-$	2-propanol/H_2O:5/1 405 torr CO T ∿85°C	Soln. orange-yellow; 0.94 torr CO_2 after 18h, no H_2; brown material isolated after rxn: $Rh(CO)_2(mnt)^-$
$RhCl_2(CO)_2^-$	HOAC/HCl/H_2O:4/1/1 $SnCl_4/SnCl_2$/Rh:83/83/1 397 torr CO T ∿ 90°C	Soln. yellow-brown; 13.8 torr CO_2 after 3 days, no H_2
$[RhCl(CO)_2]_2$ or $RhCl_2(CO)_2^-$	HOAC/HCl/H_2O:17/2/20 396 torr CO T ∿ 85°C	Deep red catalytic activity; ∿1/1 CO_2/H_2 #t = 1.06 mmoles product/mmole Rh/h
$PtCl_2(dppm)$	H_3PO_4(HI)H_2O:17/2/20 392.5 torr CO T ∿ 80°C	No catalysis
$PdCl_6^{2-}$	H_3PO_4/HCl/H_2O:17/2/20 494 torr CO T ∿ 95°C $SnCl_4/PdCl_6^{2}$:30/1	Light red soln.; 12.2 torr CO_2 after 3 days, no H_2
$PdCl_2$	H_3PO_4/HCl/H_2O: 501.5 torr CO $SnCl_2/SnCl_4/PdCl_2$:15/11/1	No catalytic activity
$[Bu_4N][Pt_2Cl_4(CO)_2]$	H_3PO_4/HCl/H_2O:4/1/1 401 torr CO T ∿ 95°C	Light yellow soln. which darkens as catalysis proceeds in Pt metal plating out; 5.8 torr CO_2 after 2 days, 6.5 torr H_2 after 2 days
$[Ir(cod)Cl]_2$ cod = 1,5-cyclo-octadiene	H_3PO_4/HI/H_2O:17/2/20 476 torr CO T ∿ 90°C ⟶ 135°C	Dark orange soln.; 10.8 torr CO_2 after 6 days, 10.7 torr H_2 after 6 days

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